V. "Notes of Researches on the Poly-Ammonias."—No. V. Action of Bichloride of Carbon on Aniline. By A. W. HOFMANN, Ph.D., F.R.S. &c. Received June 17, 1858.

In two former notes I have described the deportment of aniline as the prototype of primary monamines with the bromine- and chlorine-compounds of biatomic and triatomic radicals. It was found that under the influence of these agents, two equivalents of aniline coalesce to a more complex molecule, retaining the chemical character of the constituents; the action of bibromide of ethylene and chloroform producing respectively—

Diethylene-diphenyl-diamine $C_{32}H_{18}N_2 = \left\{ \begin{matrix} (C_4H_4)_2'' \\ (C_{12}H_5)_2 \end{matrix} \right\} N_2$.

Formyl-diphenyl-diamine .. $C_{26}H_{12}N_2 = \left\{ \begin{matrix} (C_2H)''' \\ (C_{12}H_5)_2 \\ H \end{matrix} \right\} N_2$.

The result of these experiments led me to examine the behaviour of aniline under the influence of organic chlorides containing even a larger number of chlorine equivalents. The agent selected was the body well known by the name of bichloride of carbon, *i. e.* tetra-chlorinetted marsh-gas, or chloroform, in which the residuary equivalent of hydrogen is replaced by chlorine.

Aniline and bichloride of carbon do not act upon each other at the common temperature; at the temperature of boiling water a change is perceptible, but even after several days' exposure the reaction is far from being complete. On submitting, however, a mixture of $3\frac{1}{2}$ parts by weight of aniline and 1 part of bichloride of carbon, both in the anhydrous state, for about thirty hours to a temperature of 170° C., the liquid will be found to be converted into a black mass, either soft and viscid, or hard and brittle, according to time and temperature.

This black mass, which adheres firmly to the tubes in which the reaction has been accomplished, is a mixture of several bodies. On exhausting with water, a portion dissolves, while a more or less solid resin remains behind.

The aqueous solution yields, on addition of potassa, an oily precipitate containing a considerable portion of unchanged aniline; on boiling this precipitate with dilute potassa in a retort, the aniline distils over, whilst a viscid oil remains behind, which gradually

solidifies with a crystalline structure. Washing with cold alcohol and two or three crystallizations from boiling alcohol render this body perfectly white and pure, a very soluble substance of a magnificent crimson colour remaining in solution.

The portion of the black mass which is insoluble in water dissolves almost entirely in dilute hydrochloric acid, from which solution it is reprecipitated by the alkalies in the form of an amorphous pink or dingy precipitate soluble in alcohol with a rich crimson colour. The greater portion of this body consists of the same colouring principle which accompanies the white crystalline substance. On the other hand, considerable quantities of this crystalline body are occasionally present in the product insoluble in water.

The crystalline body is insoluble in water, difficultly soluble in boiling alcohol, soluble in ether. From the hot alcoholic solution it crystallizes slowly on cooling in elongated four-sided plates, often grouped round a common centre; this substance is a well defined base; it freely dissolves in acids, from which, on the addition of the alkalies, it is thrown down as a dazzling white precipitate.

The analysis of this new base has led to the expression

$$C_{38}H_{17}N_3,$$

a formula corroborated by the analysis of a fine, somewhat difficultly soluble hydrochlorate,

$$C_{38}H_{17}N_3, HCl,$$

which is obtained by dissolving an excess of the new base in hot diluted hydrochloric acid, when it crystallizes on cooling.

A further confirmation was furnished by the examination of a bright yellow platinum-salt,

$$C_{38}H_{17}N_3, HCl, PtCl_2.$$

Both the hydrochlorate and the platinum-salt are extremely soluble in an excess of hydrochloric acid, which has therefore to be carefully avoided in their preparation.

The phase of the action of bichloride of carbon on aniline, which gives rise to the formation of the new base, is expressed by the equation

$$6C_{12}H_7N + C_2Cl_4 = C_{38}H_{17}N_3, HCl + 3(C_{12}H_7N, HCl).$$

What is the constitution of the new body? It is obviously derived from 3 molecules of aniline from which 4 equivalents of hydrogen have been eliminated by the 4 equivalents of chlorine in the bi-

chloride, the carbon entering as a biatomic molecule into the complex atom. The new body would thus become a triamine,

$$\left.\begin{matrix} C_2'' \\ (C_{12}\,H_5)_3 \\ H_2 \end{matrix}\right\} N_3.$$

It is however more probable that the carbon replaces in the form of cyanogen, when the new compound appears in the light of a diamine, as

$$\text{Cyan-triphenyl-diamine } \left.\begin{matrix} C_2\,N \\ (C_{12}\,H_5)_3 \\ H_2 \end{matrix}\right\} N_2.$$

The new compound thus becomes closely allied to melaniline, which may be viewed as diphenyl-cyan-diamine,

$$\text{Melaniline } C_{26}\,H_{13}\,N_3 = \left.\begin{matrix} C_2\,N \\ (C_{12}\,H_5)_2 \\ H_3 \end{matrix}\right\} N_2.$$

It deserves to be noticed, that in its appearance, and in its general characters, cyan-triphenyl-diamine resembles melaniline in a remarkable manner.

If we are entitled to view the new body which forms the subject of this note as a cyanogen-substitute, we have not less than four well-defined diamines of the phenyl-series.

$$\text{Diethylene-diphenyl-diamine } \left.\begin{matrix} (C_4\,H_4)''_2 \\ (C_{12}\,H_5)_2 \end{matrix}\right\} N_2.$$

$$\text{Formyl-diphenyl-diamine } \ldots\ \left.\begin{matrix} (C_2\,H)''' \\ (C_{12}\,H_5)_2 \\ H \end{matrix}\right\} N_2.$$

$$\text{Cyan-diphenyl-diamine } \ldots\ldots\ \left.\begin{matrix} C_2\,N \\ (C_{12}\,H_5)_2 \\ H_3 \end{matrix}\right\} N_2.$$

$$\text{Cyan-triphenyl-diamine } \ldots\ldots\ \left.\begin{matrix} C_2\,N \\ (C_{12}\,H_5)_3 \\ H_2 \end{matrix}\right\} N_2.$$

I intend to continue the inquiry still further in this direction, and propose next to examine the deportment of aniline with the so-called protochloride ($C_4\,Cl_4$) and sesquichloride of carbon ($C_4\,Cl_6$).